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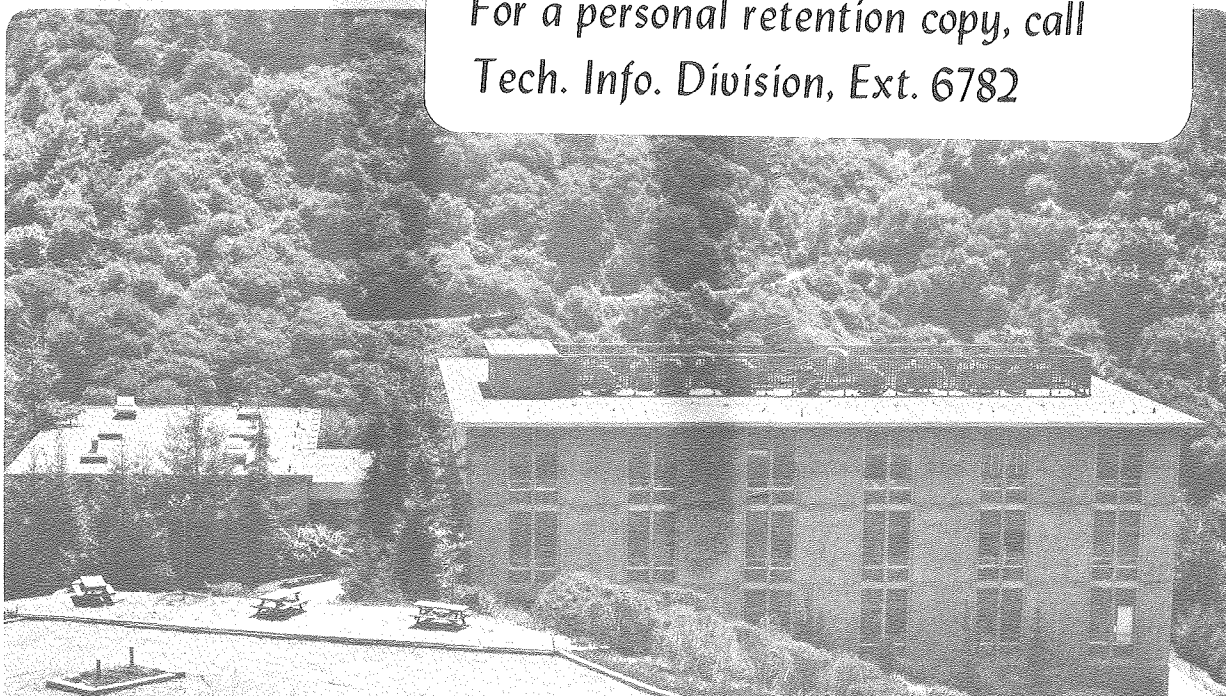
THE STRUCTURE AND INTERDIFFUSIONAL DEGRADATION OF ALUMINIDE
COATINGS ON OXIDE DISPERSION STRENGTHENED ALLOYS

D.H. Boone, D.A. Crane, and D.P. Whittle

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THE STRUCTURE AND INTERDIFFUSIONAL DEGRADATION OF
ALUMINIDE COATINGS ON OXIDE DISPERSION STRENGTHENED
ALLOYS

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A study of the effects of oxide dispersion strengthened (ODS) superalloy composition and coating processing on the structure and diffusional stability of aluminide coatings was undertaken. Increasing substrate aluminum content results in the formation of a more typical nickel base superalloy aluminide coating structure that is more resistant to spallation during high temperature isothermal exposure. The coating application process also affected coating stability, a low aluminum, outward diffusion type resulting in greater apparent stability. A SEM deep etching and fractography examination technique was used in an attempt to establish the location and kinetics of void formation. Aluminide protective lifetimes are still found to be far short of the alloys mechanical property capabilities.

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy under Contract Number W-7405-ENG-48.

1. INTRODUCTION

In the quest for materials with improved mechanical properties at elevated temperatures, particularly for use in combustion type energy conversion systems, the use of many metallurgical strengthening mechanisms has been explored. One of these, oxide dispersion strengthening (ODS), has shown considerable initial promise for providing strengthening at very high temperatures up to $\sim 0.9 T_m$ and more recently, in combination with other more conventional strengthening mechanisms, for providing intermediate temperature strength as well. The history and accomplishments of these developments is well documented in the literature^(eg. 1,2) and active investigation continues⁽³⁾.

One problem encountered early in the development, and apparently continuing to the present, is the instability of protective coatings on these alloys containing fine particle dispersions. For most ODS alloy compositions developed thus far, the use of some protective coatings is required, particularly considering the potentially expanded temperature range and lifetimes of the improved strength systems⁽³⁾.

Early test of aluminide and duplex chromium aluminide diffusion coatings identified void formation and more rapid substrate interdiffusion as the mechanism of premature coating spallation and failure. This premature failure mode has apparently continued to occur despite the introduction of new coating systems such as the overlays and duplex overlay-diffusion systems.

Of the limited attention given to the behavior of coatings on ODS alloys much of the testing has focused on the resulting protective lifetime and not on the mechanism of coating failure or the interaction of type of

coating and substrate composition. It was observed in one study that substrate composition could be important in that the tendency among ODS alloys to form porosity decreased with increasing alloy oxidation resistance⁽³⁾.

This paper reports the results of a limited study of the effect of nickel base ODS substrate composition, primarily aluminum level, but also other alloy strengthening additions and type of aluminizing treatment, high activity inward type and low activity outward type⁽⁴⁾, on the initial coating structure and subsequent diffusional stability. Recent studies have demonstrated the apparent superiority of overlay type coatings when compared with the more simple diffusion aluminum type aluminides. However, it should be noted that since one mode of overlay coating degradation is aluminum interdiffusion between the coating and the substrate forming an in-situ aluminide coating with the potential for diffusional instability, a better understanding of the critical factors involved with the aluminide formation is important for the use of overlay coatings as well.

2. EXPERIMENTAL

The composition of the wrought nickel base ODS alloys used in this study are given in Table 1. Suitably prepared samples surface ground with 600 grit paper, were coated together in either of the two coating processes studied as follows:

High aluminum activity process - 700°C/2h in pack followed by 1080°C/4h diffusion treatment.

Low aluminum activity process - 1000°C/6h above the pack, no subsequent diffusion treatment.

As-processed samples were prepared for examination by standard metallographic techniques, additional samples were fractured and examined using the SEM. Selected metallographically prepared samples were deep etched using techniques described elsewhere⁽⁵⁾ in an attempt to better identify size and location of coating void formation.

System oxidation and diffusional stability were studied after isothermal exposure in air at 1180°C for periods of 6 to 276h. Structural examination techniques described above were also used.

3. RESULTS

Figure 1 shows a comparison of the as-processed inward growth type aluminide coating microstructure on the ODS alloys listed in Table 1. The difference in total coating thickness, increasing with increasing aluminum content (and substrate alloy strengtheners) is discussed below. Coating spallation at the coating-substrate interface is evident in the 0.6% and 4.5% Al alloys. Some void formation is also visible in the 4% and 8.5% Al content alloys as well. The 0% Al alloy has a typical three zone inward type aluminide structure with the one feature of the inner zone being very thin, consisting of a semi-continuous layer of substrate elements, presumably chromium and/or chromium carbides. With increasing substrate aluminum content (and possibly other elements which affect the γ' - β phase boundary) the inner coating zone is generally observed to be larger with a more dispersed distribution of refractory metal rich precipitates.

Potentially anomalous results are seen for the MA 754 (0.6% Al) and MA 6000 E (4.5% Al). It is not known, however, whether the 0.6% Al is present in solution or as an inert Al_2O_3 precipitate which aggravates the potential for void formation because of the higher level of inert dispersant

Figure 2 presents a comparison of the as-processed, outward growth type aluminide coating microstructure on the ODS alloys. The 0% Al alloy has no coating evident indicating either extreme instability or low coating rate. The 4% Al alloy lost its coating at some point during or directly after the coating process. Voids are quite evident in the 0.6% Al alloy with somewhat fewer voids in the 4.5% and 8.5% Al alloys respectively. The presence of voids in the as-coated systems portends the lack of stability of the coating during further exposure at higher temperatures.

Figure 3 shows the void formation which results from 1180°C air exposures of the outward type aluminide coated MA 6000 E (4.5% Al). Rapid void formation is evident at the coating substrate interface in the first 6 hours of exposure, as is aluminum diffusion into the substrate and γ' phase precipitation. The rate of void formation and interdiffusion appear to follow some type of parabolic diffusional kinetics until at 275 hours the coating begins to spall.

The structure of a 4.5% Al (MA 6000E) substrate with an outwardly grown coating exposed for 100h at 1180°C is shown in Fig. 4. Deep etch removal of the coating shows the voids in the inner zone and at the coating substrate interface. The gradient of γ' phase precipitate from aluminum diffusion into the substrate is also clearly shown. For this examination of void location, the deep etching technique was found to be indecisive and a fractography technique was employed instead. Fractographs as illustrated in Figures 5 and 6 clearly show the location of voids in the coating. The voids appear concentrated at the imaginary interface between the inner and outer coating zone and extend through the inner coating zone with another zone of void precipitation occurring at the coating substrate interface.

Several differences between the inward and outward type coatings are seen with the fine grained β (NiAl) fracture in the outer zone of the inward type coating in Figure 5, and the coarse grain fracture in the phase pure β (NiAl) phase in the outer zone of the outward type coating in Figure 6.

4. DISCUSSION

Although some variability in coating structure existed even with the same specimen it is possible to distinguish trends and effects of the variables investigated. No effect of substrate orientation with respect to strong working and recrystallization textures were seen in this study when specifically looked for.

The effect of aluminum on the structure of the inner coating zone was expected and predictable from earlier coating studies. Low aluminum content nickel base ODS alloys exhibited structures similar to those observed on aluminum free cobalt base alloys where coatings must be kept thin to preclude premature spallation at the inner coating zone-substrate interface.

Since the β (NiAl) phase in the inner coating zone results from the removal of nickel from this region by essentially 100% Ni diffusion in hypostoichiometric β (NiAl), the higher substrate aluminum levels result in a larger amount of β phase for a given volume removal of nickel. Any effect of substrate alloying elements in moving the γ' - β phase limit to lower nickel levels would result in a further increase in amount of β phase formed in this zone. Comparison of the low alloy 4% Al (YD NiCrAl) and the higher alloyed but only slightly higher aluminum content MA 6000 E (4.5%Al) indicates an apparent effect of the other alloying elements. Since β (NiAl) has only limited solubility for most other elements, the other substrate alloying elements are precipitated and grow inward as the interface of the β (NiAl) phase inward. The insoluble oxide dispersants are also concentrated in this region as well as in the outer layer of the inward type coating.

The formation of voids associated with the coating of ODS alloys has been attributed to Kirkendal porosity resulting from the almost unidirectional movement of nickel and aluminum in these system. Nickel diffusing out through the β (NiAl) can result in the precipitation of vacancies at the initial interface and continue through the inner coating zone as it grows, the presence of precipitates and oxide dispersions in this zone presumably acting as nucleation sites for the void formation. In spite of this unique diffusional nature of the aluminides, these voids are not generally seen for identical coatings applied to similar composition nickel base alloys which do not contain oxide dispersants. Presumably in those systems the volume changes associated with the precipitates of the low solubility refractory metal rich phases, or some other mechanism compensates in some manner for the vacancy flux across the inward moving coating interface. Voids or coating separation are found in low aluminum level and lean alloy substrates, free of inert dispersions, as previously noted. The presence and concentration of the oxide dispersants in the inner zone must, therefore, be the key to the void nucleation.

The formation of voids in uncoated ODS alloys and the extremely rapid interdiffusion of certain elements have been observed and discussed elsewhere⁽³⁾. One indication that diffusion rate may also be important is the observation of the apparently reduced void formation kinetics in the slower growing lower activity outward type coatings. However, inner coating morphology could also be having an effect.

The extent of aluminum diffusion from the inner coating layer into the substrate is excessive when compared with standard nickel base superalloy coating stability and is certainly related to the rapid interdiffusion

observed elsewhere for the ODS alloys. Although not a part of this study, cursory examination of the protective oxide which forms on the outwardly grown coating during exposure, Fig. 4, revealed no differences from that formed on a similar coating applied to other superalloy substrates⁽⁶⁾. However, an oxide formed on an inward type coating containing a very fine dispersion of the oxide dispersion strengtheners Al_2O_3 , ThO_2 or Y_2O_3 has been postulated to exhibit an improved adherence and will be examined in more detail in a continuing study. Likewise the effect of these dispersions on the oxidation behavior of the uncoated alloys, many of them Al_2O_3 formers, deserves further attention in future studies.

5. CONCLUSIONS

1. The thickness and structure of aluminide coatings particularly the inner coating zone on ODS alloys is a strong function of substrate alloy composition. Increased aluminum levels and possible refractory strengthening elements appear to be beneficial.
2. The structure and stability of aluminide coatings on ODS alloys is a function of the coating type and deposition process.
3. Coating void formation and the resulting spallation occurs in the inner coating zone and is delayed but not prevented by a larger more dispersed zone produced by outward type coatings on high aluminum content alloys.
4. For all ODS alloys and aluminide coatings studied, the coating systems appeared to have insufficient protectivity to match the available mechanical properties. The lack of stability was manifested by both coating void formation and resulting spallation and aluminum diffusion into the substrate.

ACKNOWLEDGMENT

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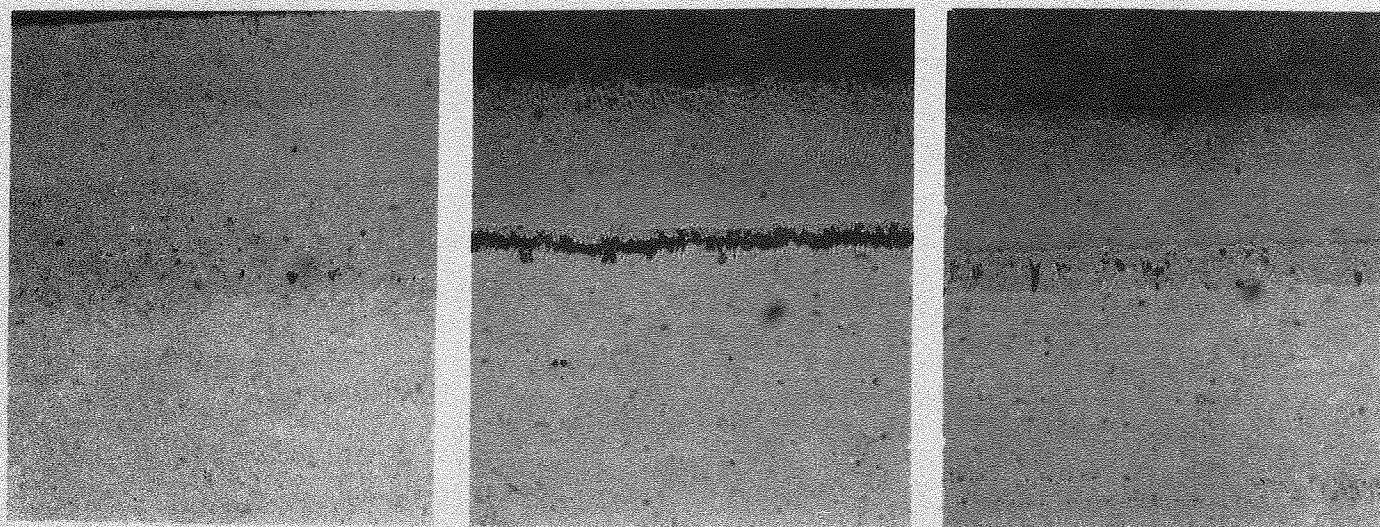
FIGURE CAPTIONS

- Figure 1 Microstructures of as-formed and diffused inward type aluminide coatings on ODS alloys with varying aluminum contents as indicated.
- Figure 2 Microstructures of as-formed outward type aluminide coatings on ODS alloys with varying aluminum contents as indicated.
- Figure 3 Microstructure of outward type aluminide coating on 4.5% Al (MA6000E) exposed at 1180°C for times indicated showing progression of void formation in inner coating zone.
- Figure 4 Use of deep etch technique to identify void location and distribution for outward type coating on 4.5% Al substrate, exposed 100h at 1180°C in air.
- Figure 5 SEM fractograph of inward type aluminide coating on 4% Al ODS alloy showing differences in coating structure.
- Figure 6 SEM fractograph of outward type aluminide coating on 4.5% Al alloy exposed 24h at 1180°C in air showing differences in coating structure and location of voids in inner coating zone.

TABLE 1

COMPOSITION OF OXIDE DISPERSION ALLOYS ALUMINIZED IN THIS STUDY

	<u>Ni</u>	<u>Cr</u>	<u>Al</u>	<u>Other</u>
DS NiCr	Bal	20	0	2% ThO ₂
MA 754	Bal	16	.6	1% Y ₂ O ₃
YD NiCrAl	Bal	16	4	0.6%Y ₂ O ₃ . .007C
MA 6000E	Bal	15	4.5	1.1Y ₂ O ₂ , 2Mo, 4W, 2Ta, 2.5Ti
Alloy 51	Bal	9.3	8.5	1.1Y ₂ O ₃ , 3.4Mo, 6.6W



8.5% Al

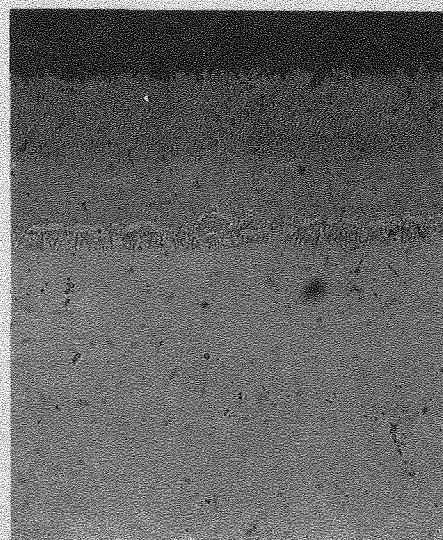
4.5% Al

4% Al

25 μ m



0.6% Al

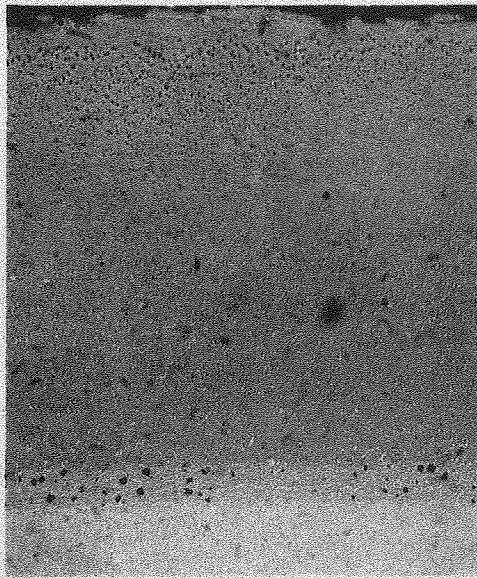


0% Al

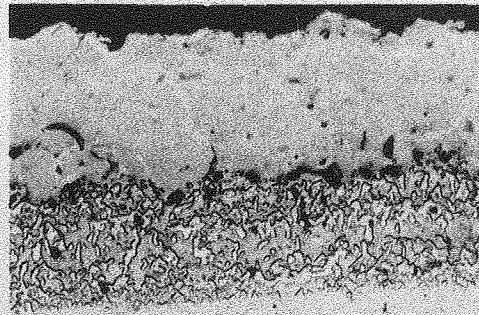
INWARD TYPE ALUMINIDE

XBB 812-1543

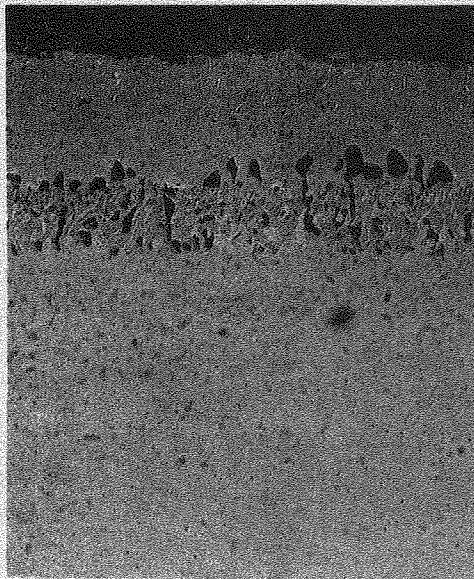
Fig. 1. Microstructures of as-formed and diffused inward type aluminide coatings on ODS alloys with varying aluminum contents as indicated.



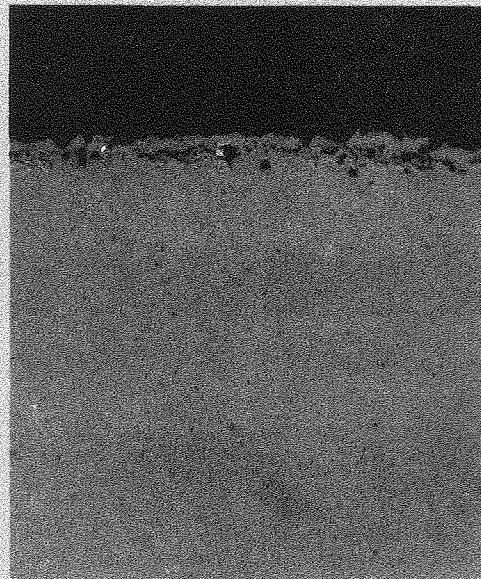
8.5% AL



4.5% AL



0.6% AL



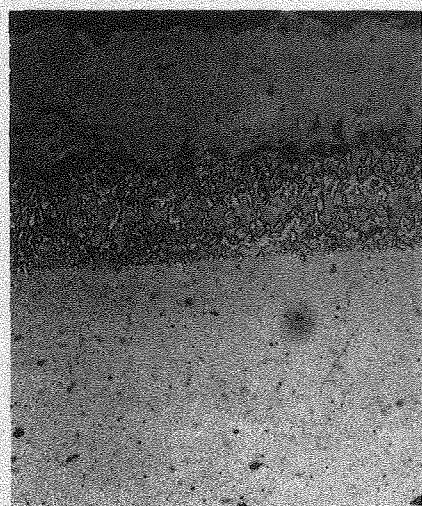
0% AL

25 μ m

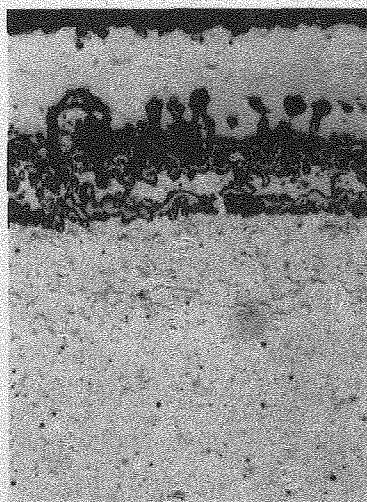
XBB 812-1540

OUTWARD ALUMINIDE COATING

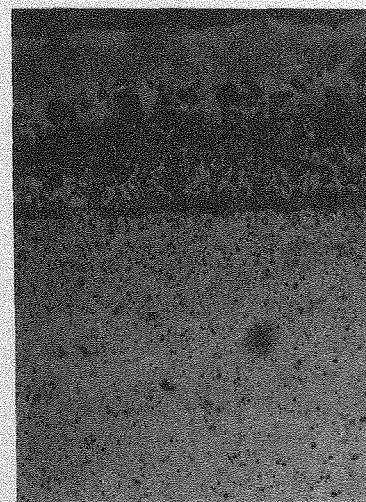
Fig. 2. Microstructures of as-formed outward type aluminide coatings on ODS alloys with varying aluminum contents as indicated.



As-Coated

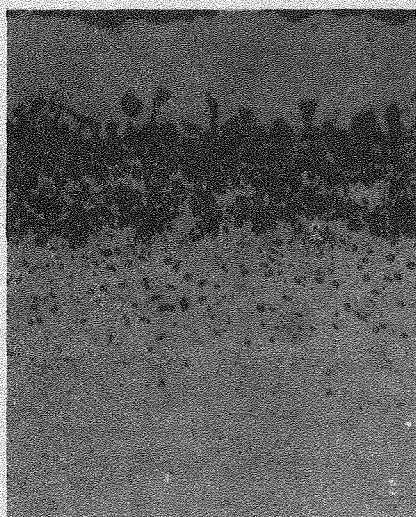


6 h

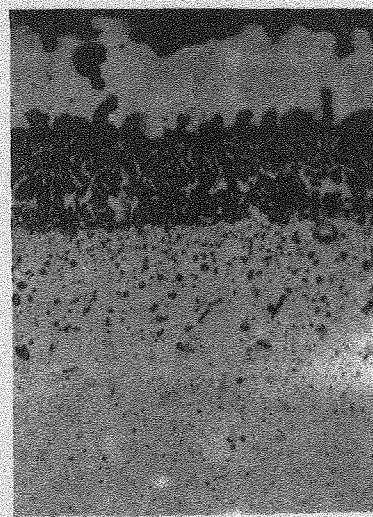


24 h

20 μ m



75 h

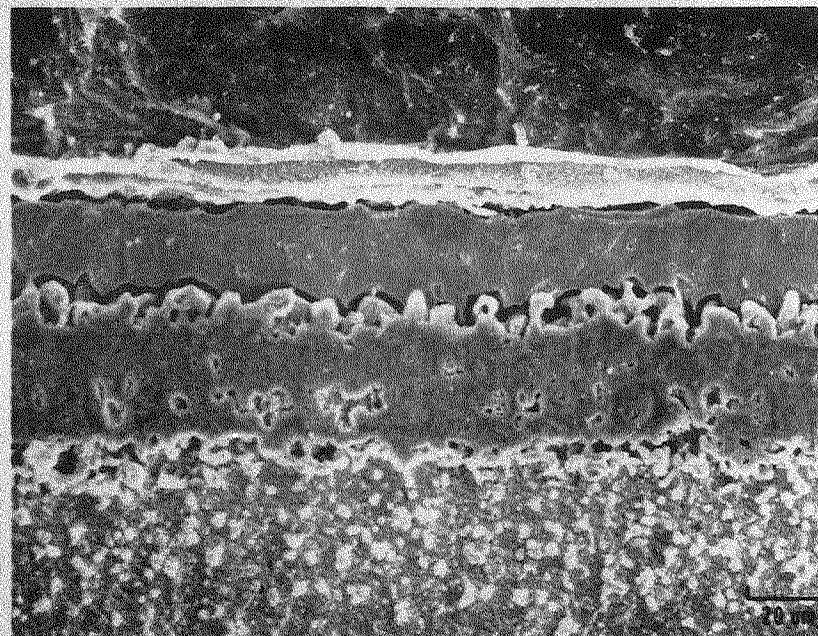
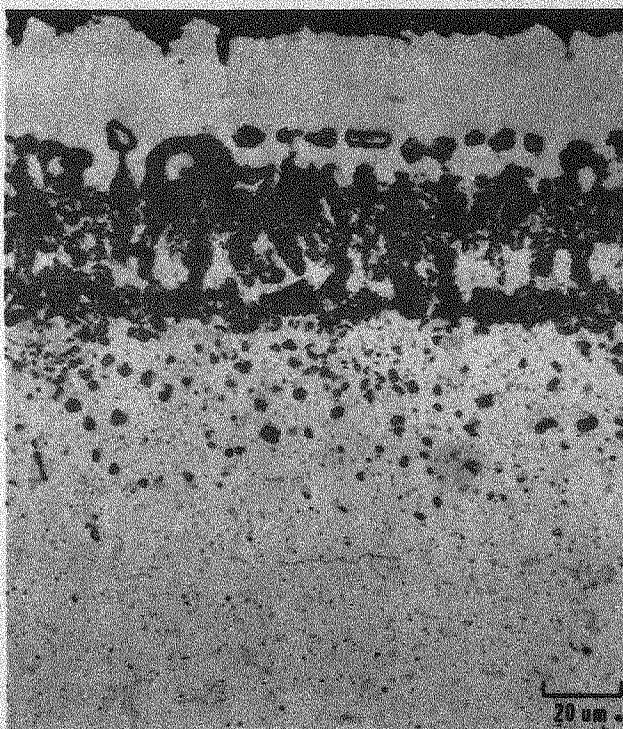


275 h

OUTWARD TYPE ALUMINIDE

XBB 812-1544

Fig. 3. Microstructure of outward type aluminide coating on 4.5% Al (MA6000E) exposed at 1180°C for times indicated showing progression of void formation in inner coating zone.



DEEP ETCH

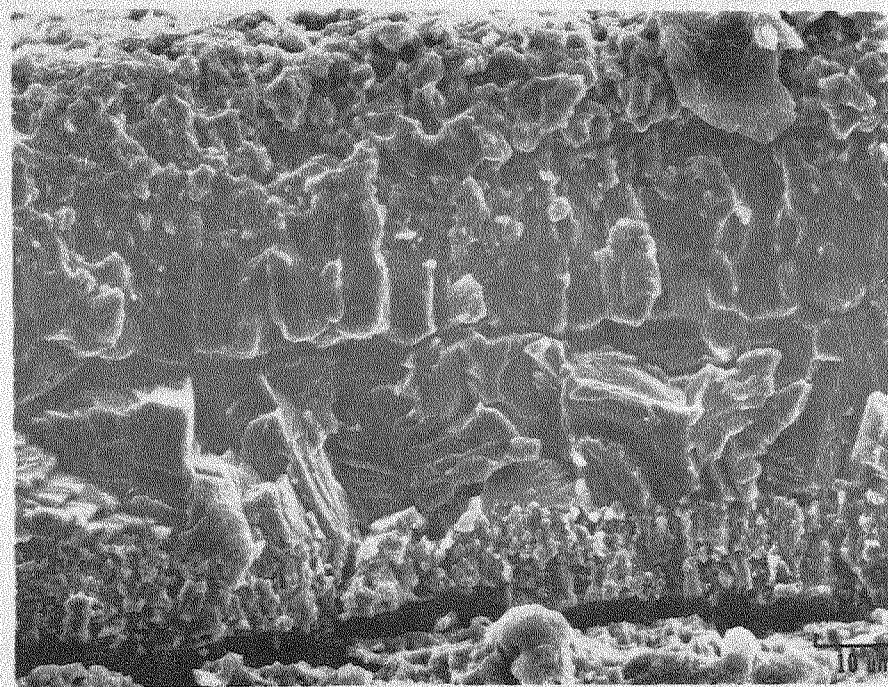
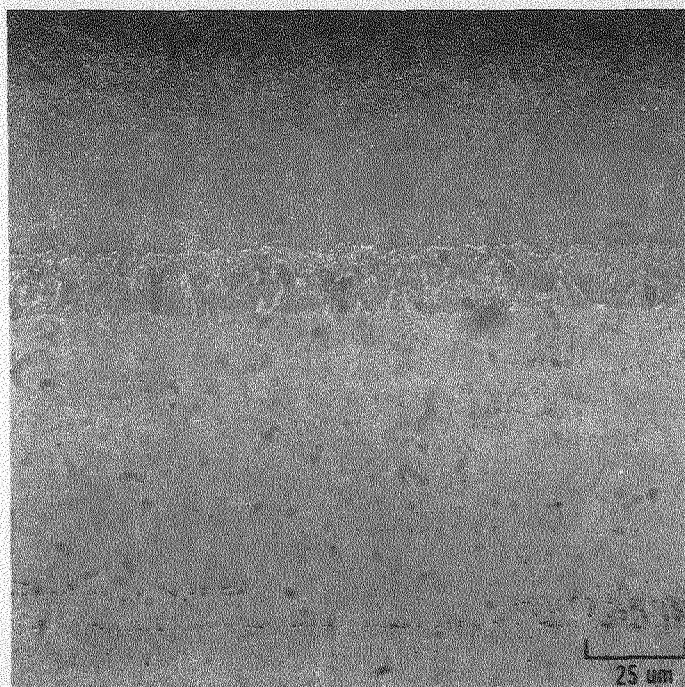
MA 6000 E

OUTWARD COATING

XBB 812-1541

1180 C/100 H

Fig. 4. Use of deep etch technique to identify void location and distribution for outward type coating on 4.5% Al substrate, exposed 100h at 1180°C in air.



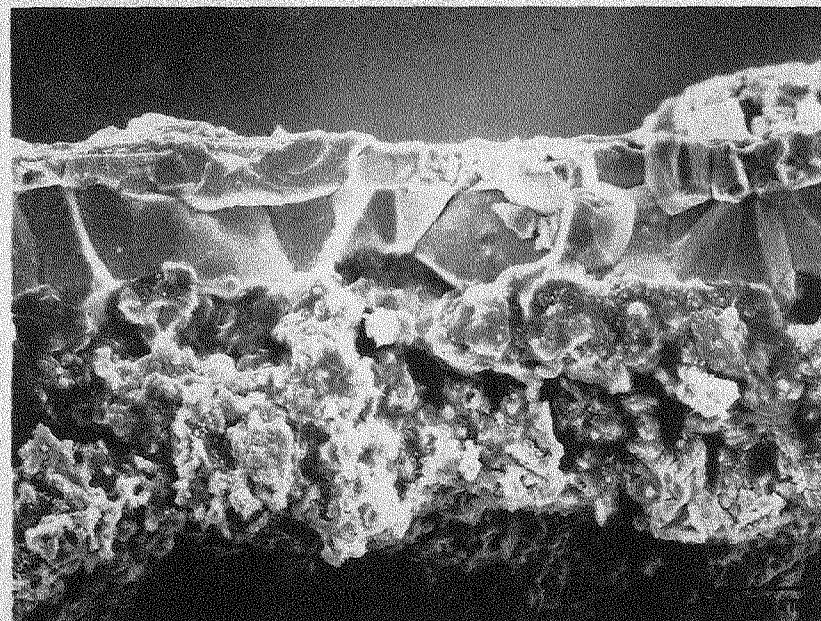
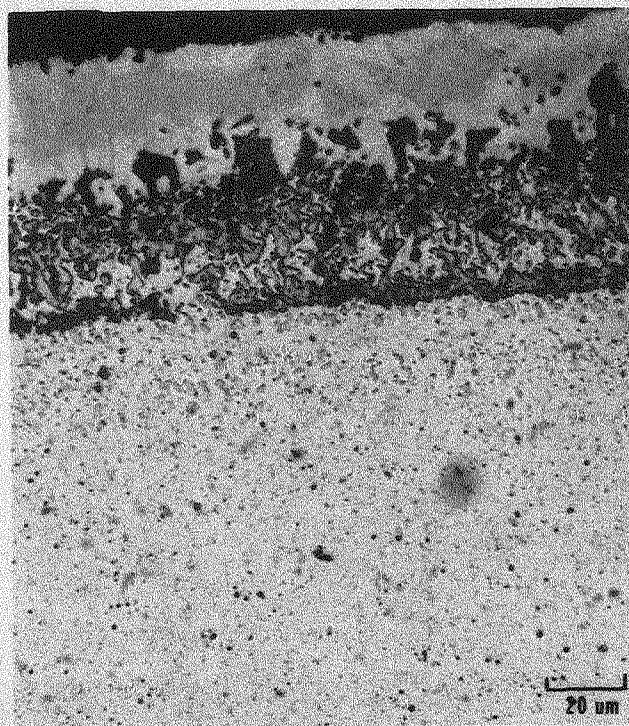
XBB 812-1517

4% Al ODS Alloy

Inward Type Coating

As Coated

Fig. 5. SEM fractograph of inward type aluminide coating on 4% Al ODS alloy showing differences in coating structure.



XBB 812-1542

4.5% AL ODS ALLOY

OUTWARD TYPE ALUMINIDE

1180 C/24 H

Fig. 6. SEM fractograph of outward type aluminide coating on 4.5% Al alloy exposed 24h at 1180 C in air showing differences in coating structure and location of voids in inner coating zone.